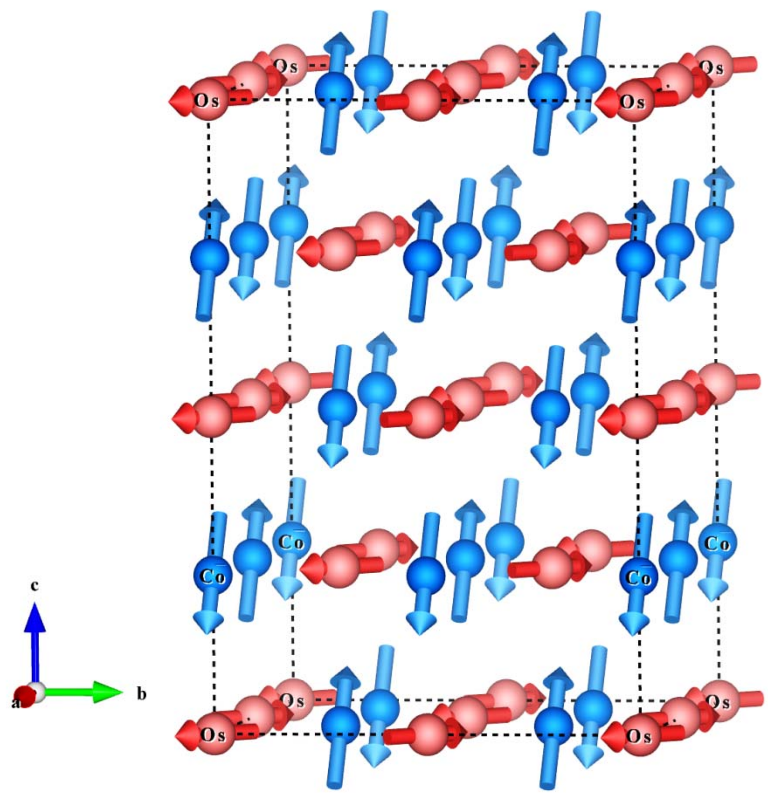
Competing superexchange interactions in osmate double perovskites



Patrick Woodward
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Outline

- Introduction
- A_2MOsO_6 with M = Mg^{2+}
- A_2MOsO_6 with M = Cr^{3+}
- A_2MOsO_6 with M = Co^{2+}
- Concluding thoughts

Combining 3d and 5d transition metals

3d transition metal oxides

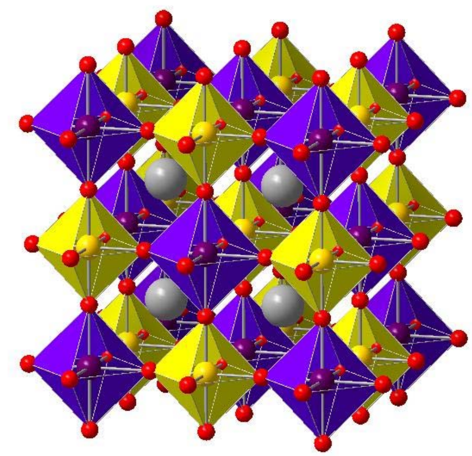
- Charge and orbital ordering
- Cooperative magnetism
- Superconductivity
- Colossal magnetoresistance

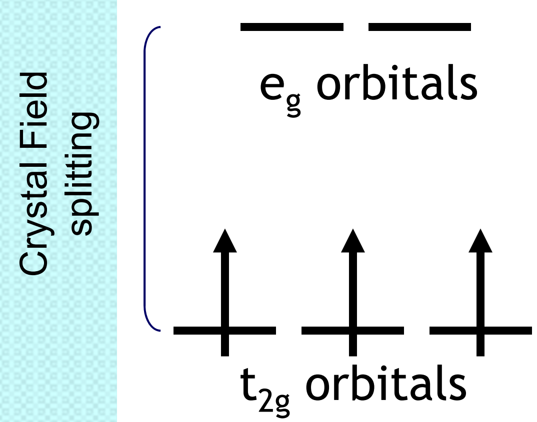
5d transition metal oxides

- Spin orbit coupling
- Itinerant electrons
- Charge density waves

A_2MOsO_6 Double Perovskites

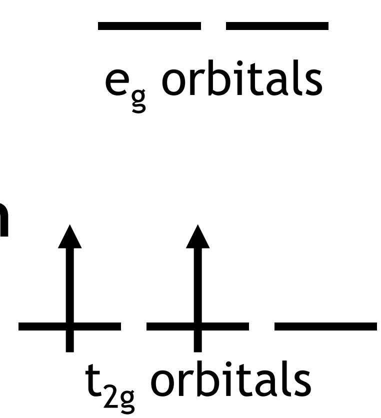
6	7	8	9	10
Cr	Mn	Fe	Co	Ni
Mo	Tc	Ru	Rh	Pd
W	Re	Os	Ir	Pt





Os^{5+}
d^3 ion

Os^{6+}
d^2 ion



A_2MOsO_6 Perovskites

A_2MOsO_6	Tol. Factor	Structure	3d cation	5d cation
Sr_2CrOsO_6	0.999	*R-3* ($a^-a^-a^-$ tilting)	Cr^{3+} (d^3)	Os^{5+} (d^3)
Sr_2FeOsO_6	0.990	*I4/m* ($a^0a^0c^-$ tilting)	Fe^{3+} (d^5)	Os^{5+} (d^3)
Sr_2ScOsO_6	0.968	$P2_1/n$ ($a^-a^-c^+$ tilting)	---	Os^{5+} (d^3)
$LaSrNiOsO_6$	0.962	$P2_1/n$ ($a^-a^-c^+$ tilting)	Ni^{2+} (d^8)	Os^{5+} (d^3)
$LaSrCoOsO_6$	0.953	$P2_1/n$ ($a^-a^-c^+$ tilting)	Co^{2+} (d^7)	Os^{5+} (d^3)
Ca_2CrOsO_6	0.945	$P2_1/n$ ($a^-a^-c^+$ tilting)	Cr^{3+} (d^3)	Os^{5+} (d^3)
Ca_2FeOsO_6	0.936	$P2_1/n$ ($a^-a^-c^+$ tilting)	Fe^{3+} (d^5)	Os^{5+} (d^3)
Sr_2NiOsO_6	0.962	*I4/m* ($a^0a^0c^-$ tilting)	Ni^{2+} (d^8)	Os^{6+} (d^2)
Sr_2MgOsO_6	0.954	*I4/m* ($a^0a^0c^-$ tilting)	---	Os^{6+} (d^2)
Sr_2CoOsO_6	0.953	*I4/m* ($a^0a^0c^-$ tilting)	Co^{2+} (d^7)	Os^{6+} (d^2)
Ca_2CoOsO_6	0.901	$P2_1/n$ ($a^-a^-c^+$ tilting)	Co^{2+} (d^7)	Os^{6+} (d^2)
Sr_2CaOsO_6	0.893	$P2_1/n$ ($a^-a^-c^+$ tilting)	---	Os^{6+} (d^2)

Sr_2MOsO_6 Synthesis

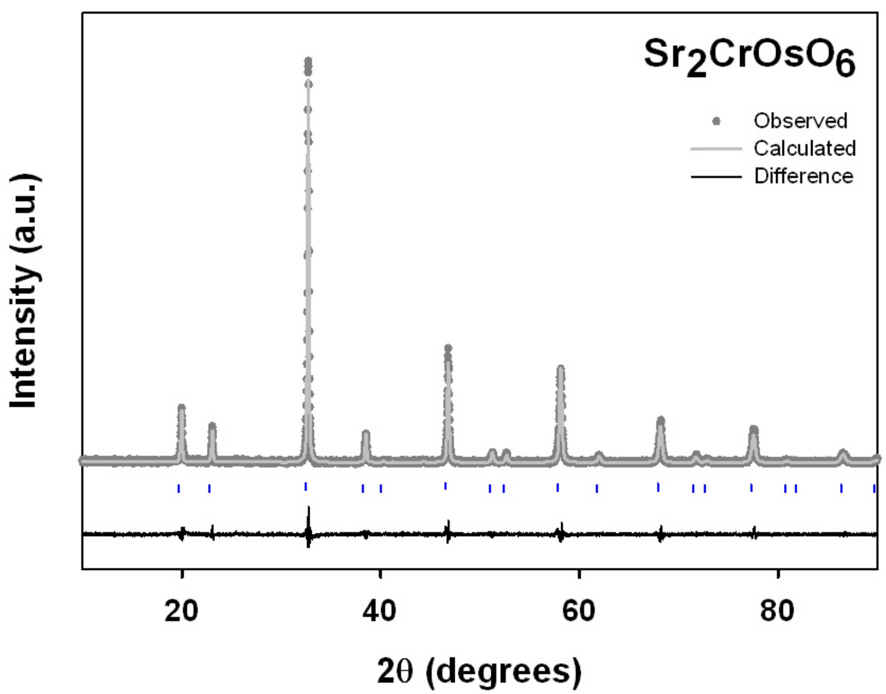
$$6\ SrO_2 + Cr_2O_3 + CrO_3 + 3\ Os \rightarrow 3\ Sr_2CrOsO_6$$

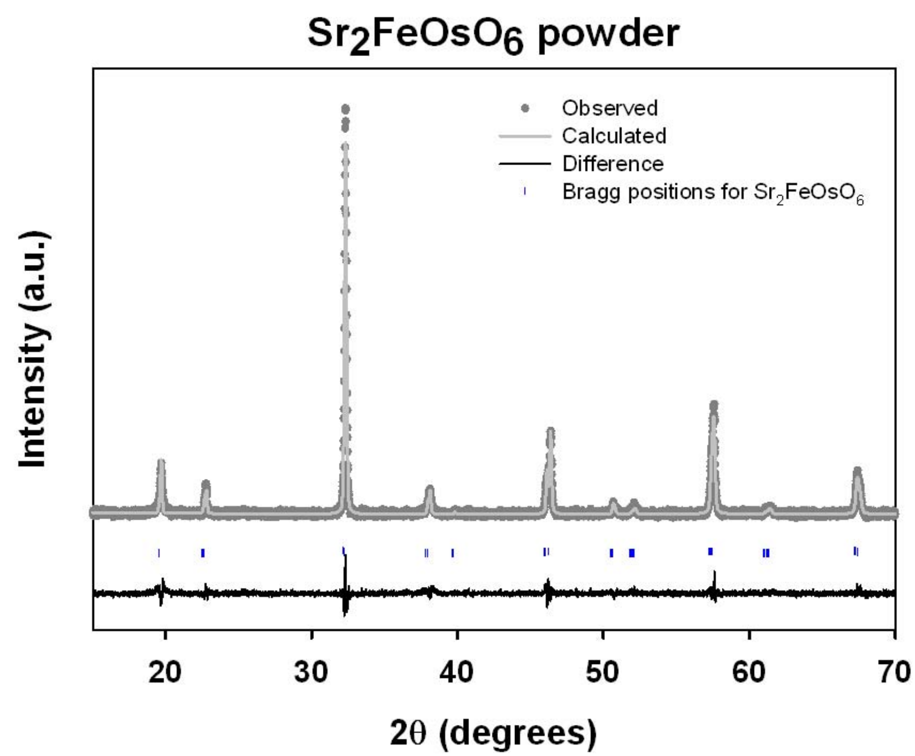
$$4\ SrO_2 + Fe_2O_3 + 2\ Os + (2\ PbO_2) \rightarrow 2\ Sr_2FeOsO_6 + 2\ PbO + ½\ O_2$$

$$4\ SrO_2 + 2\ CoO + 2\ Os + (3\ PbO_2) \rightarrow 2\ Sr_2CoOsO_6 + 3\ PbO + ½\ O_2$$

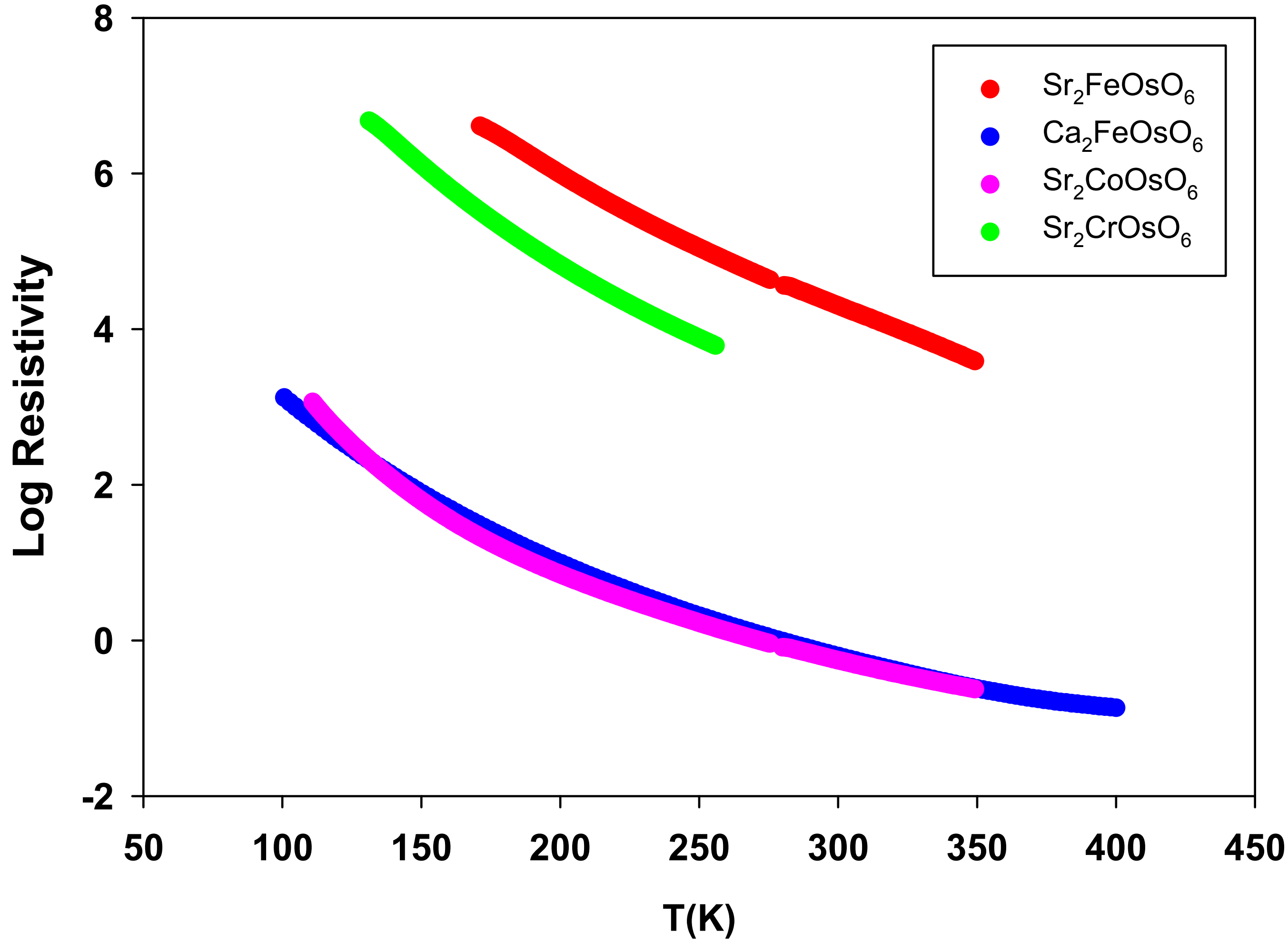
All reactions carried out in sealed silica tubes at T ~ 1000 °C

PbO_2 decomposes at high temperature and acts as an in-situ O_2 source





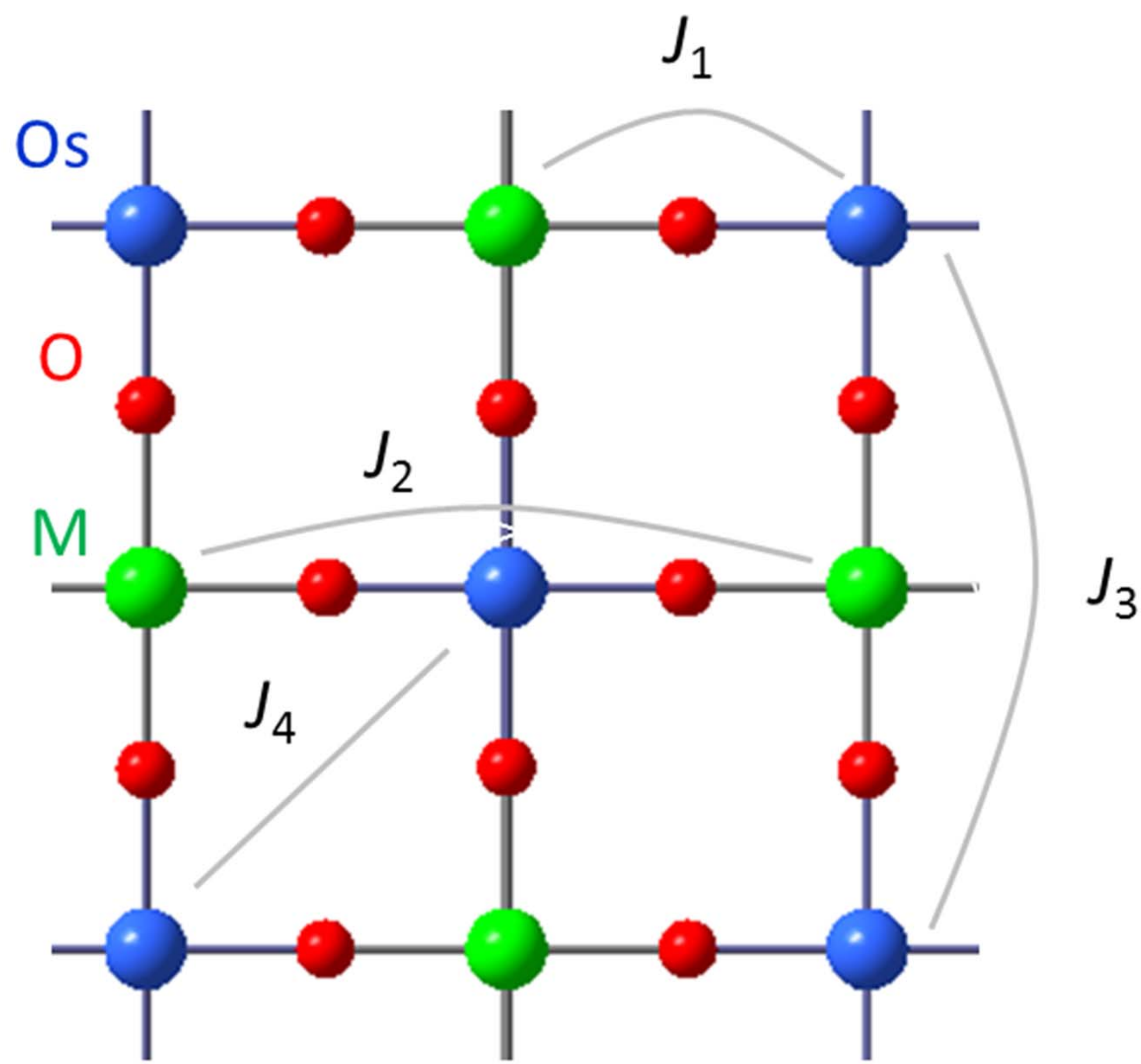
Electrical Transport



All of the samples show activated transport (variable range hopping).

Localized electron magnetism.

Superexchange interactions (3d-5d ions)



Outline

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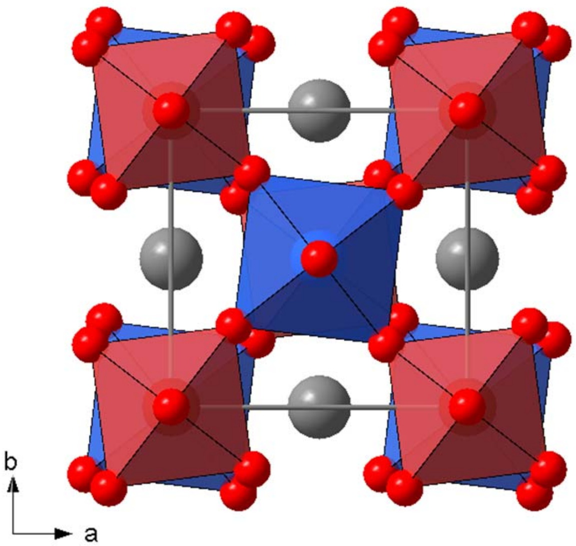
- A_2MOsO_6 with M = Cr^{3+}
- A_2MOsO_6 with M = Co^{2+}
- Concluding thoughts

Sr_2MgOsO_6 Structure



Tolerance Factor = 0.954

Space Group: *I*4/*m* (Tetragonal)

$a^0a^0c^-$ tilting

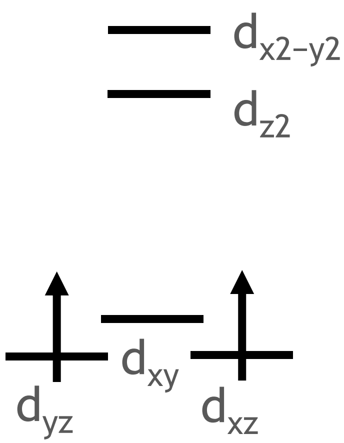
100% Mg/Os ordering

Mg^{2+}–O distances (Å)
4×2.031(1), 2×2.050(2)

Os^{6+}–O distances (Å)
4×1.910(1), 2×1.939(2)

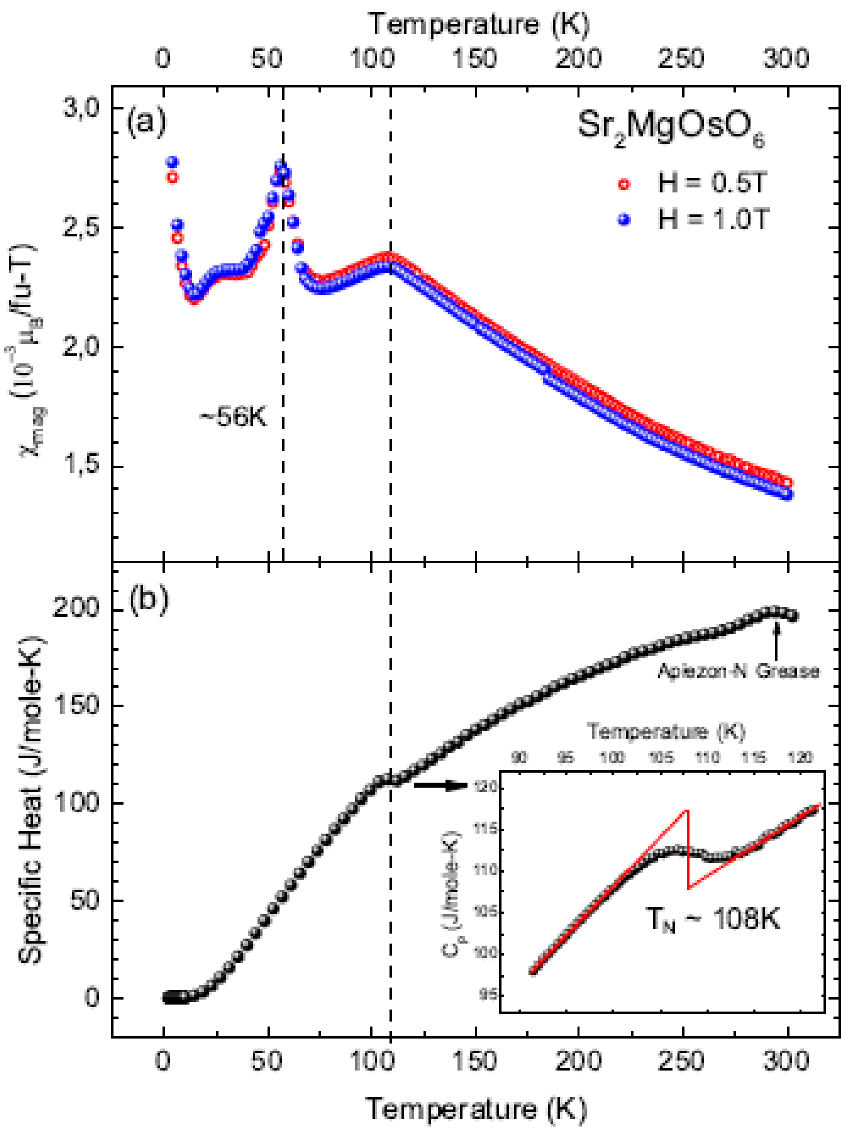
Mg–O–Os angles:
165.30(6)°, 180°

The Os octahedron shows a slight axial elongation



Os^{6+} (d^2)

Sr_2MgOsO_6 Magnetism



Curie-Weiss fit

$\mu_{eff} = 1.59\ \mu_B$

$\theta = -151$ K

The moment is reduced from spin only value ($\mu_{eff} = 2.82\ \mu_B$) by spin orbit coupling

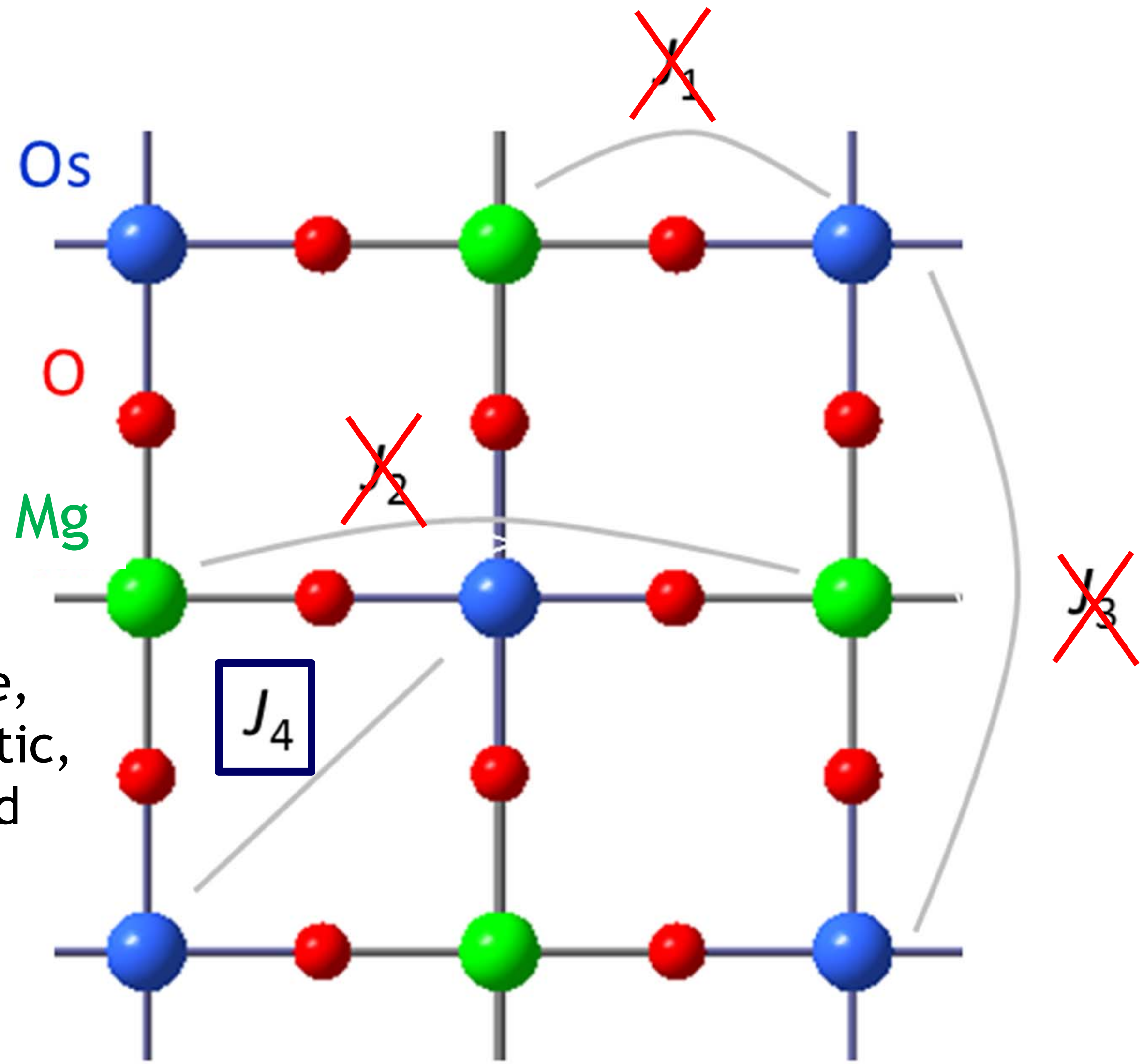
Fairly strong antiferromagnetic interactions

Neutron diffraction shows no evidence for long range magnetic order

"Spin Glass" $T_G = 108$ K

in collaboration with Sabine Wurmehl & Berndt Büchner (IFW Dresden)

Superexchange interactions (Sr_2MgOsO_6)



Non-negligible,
antiferromagnetic,
and frustrated

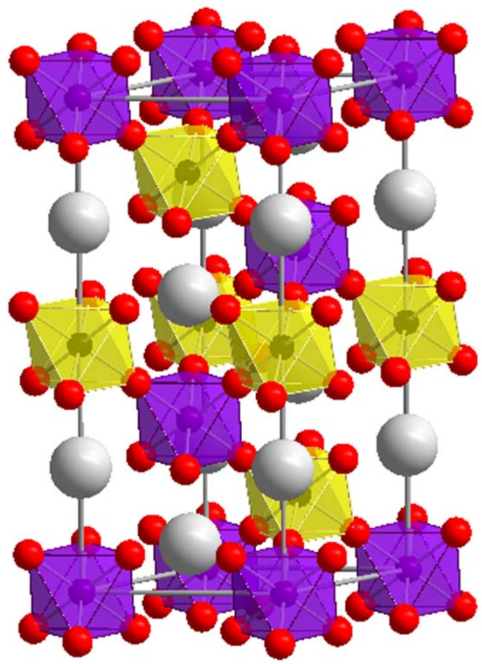
Outline

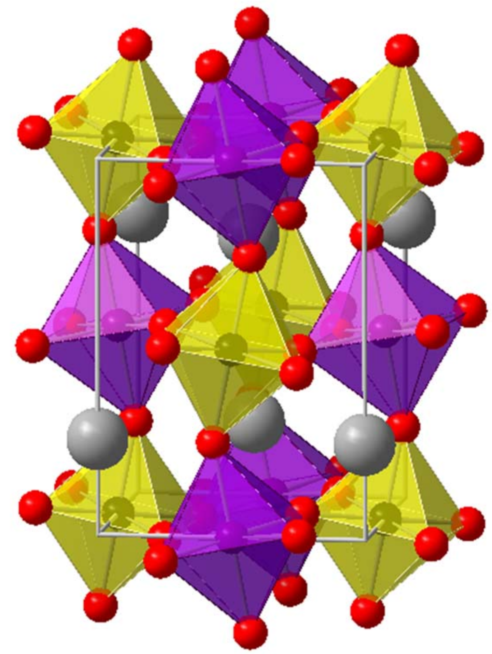
- Introduction
- A_2MOsO_6 with M = diamagnetic ion
- A_2MOsO_6 with M = Cr^{3+}
- A_2MOsO_6 with M = Co^{2+}
- Concluding thoughts

Crystal Structure

Sr_2CrOsO_6 ⟶ Ca_2CrOsO_6

chemical pressure





Tolerance Factor = 0.999

Space Group: $R\bar{3}$ (Rhombohedral)

$a^-a^-a^-$ tilting

Cr−O−Os angles = 170.34(4)°

74% Cr/Os ordering

Tolerance Factor = 0.945

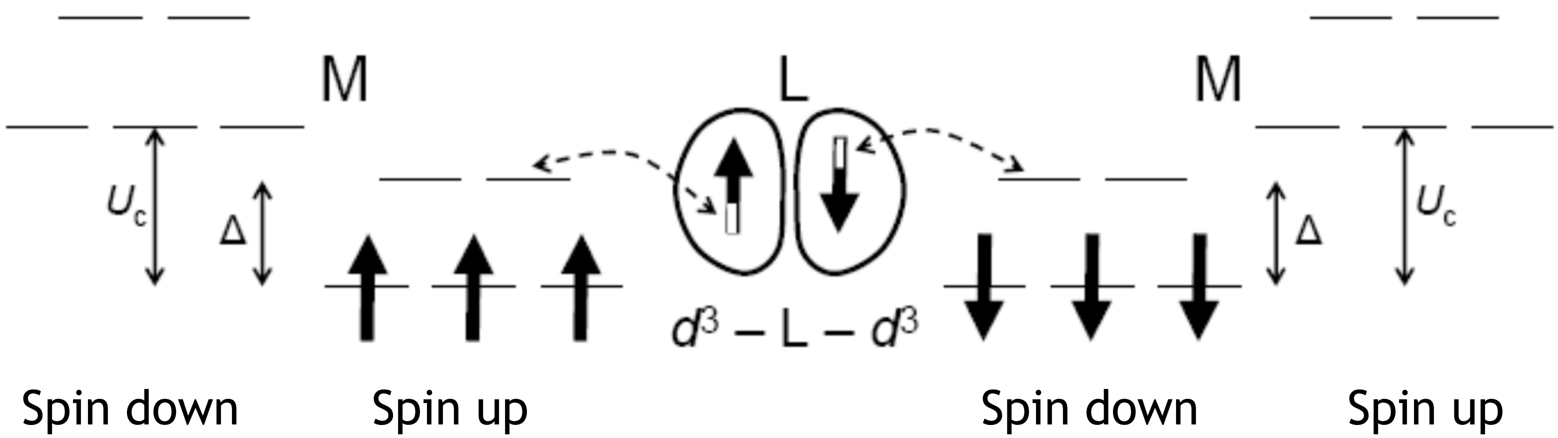
Space Group: $P2_1/n$ (Monoclinic)

$a^-a^-b^+$ tilting

Cr−O−Os angles = 152.7−153.8(1)°

74% Cr/Os ordering

d^3-d^3 superexchange



Os^{5+} O Cr^{3+}

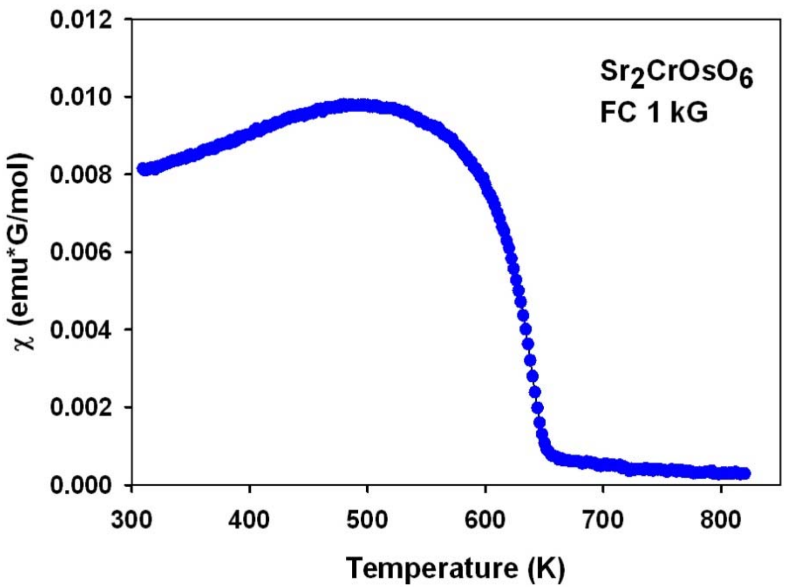
d^3 - d^3 → antiferromagnetic coupling

3d	$LaCrO_3$	G-type AFM (T_N = 320 K)
4d	$SrTcO_3$	G-type AFM (T_N = 1020 K)
5d	$NaOsO_3$	G-type AFM (T_N = 410 K)*

*Slater transition

Magnetism

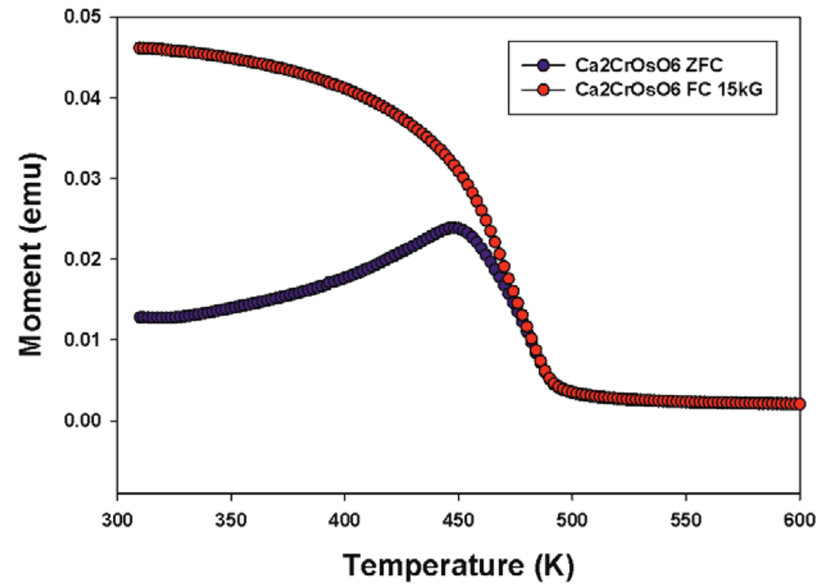
Sr_2CrOsO_6



Ferrimagnetic

$T_C \approx 660$ K

Ca_2CrOsO_6

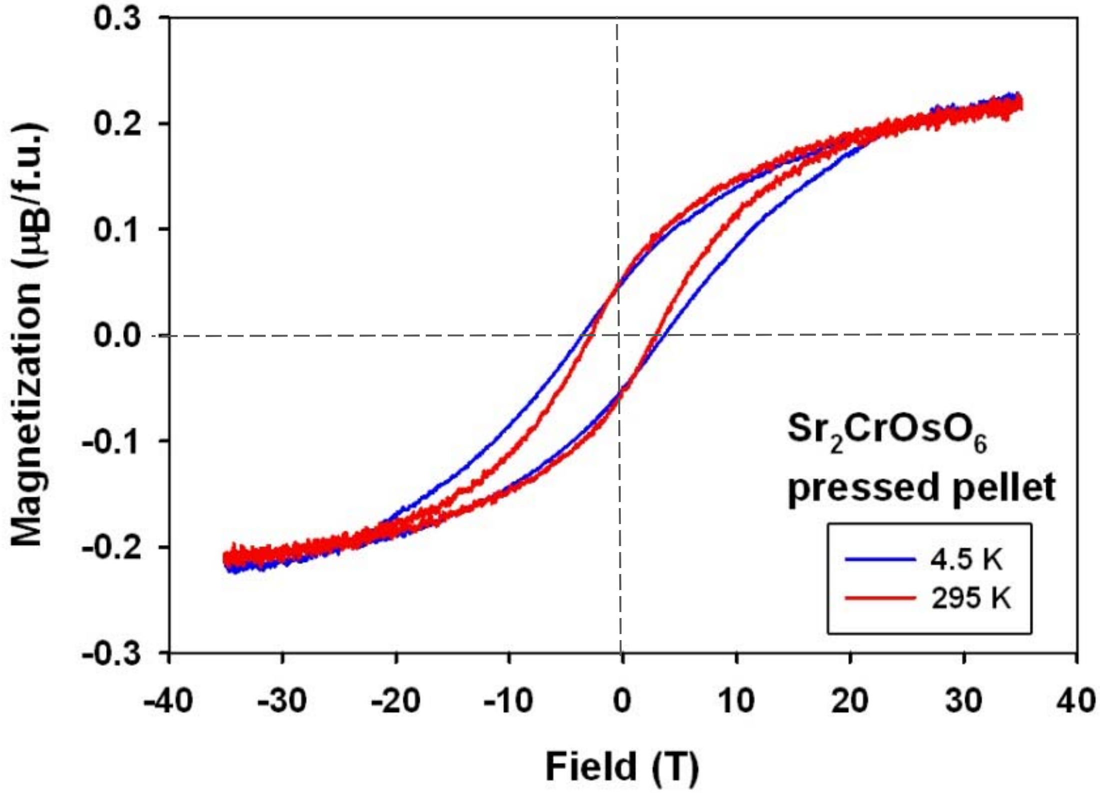


Ferrimagnetic

$T_C \approx 490$ K

The Cr−O−Os coupling (J_1) is dominant and AFM which leads to a ferrimagnetic ground state. Bending the bond angle reduces J_1 and T_C

Sr_2CrOsO_6 M vs. H



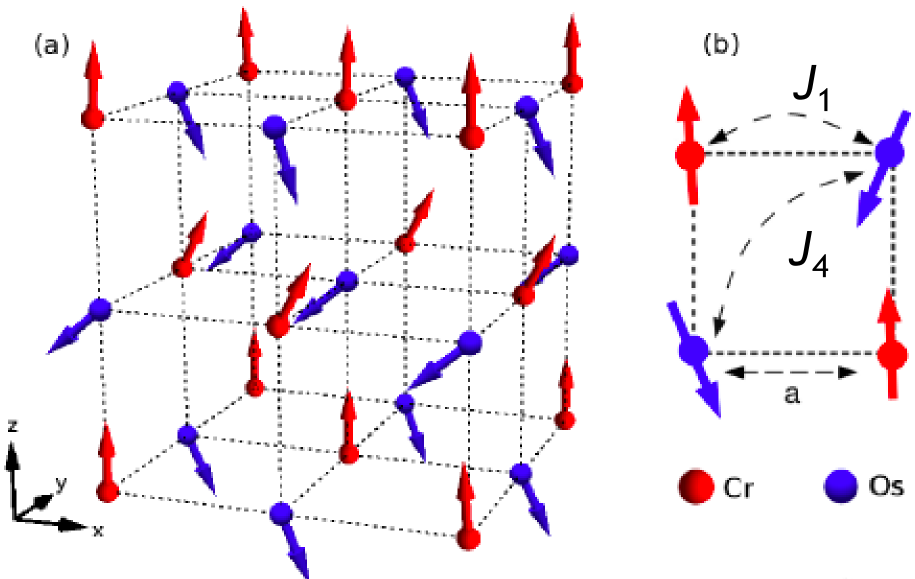
Saturation magnetization, $M_S \approx 0.22\ \mu_B$/f.u.

Coercivity, $H_C \approx 8$ T (@ 5 K)

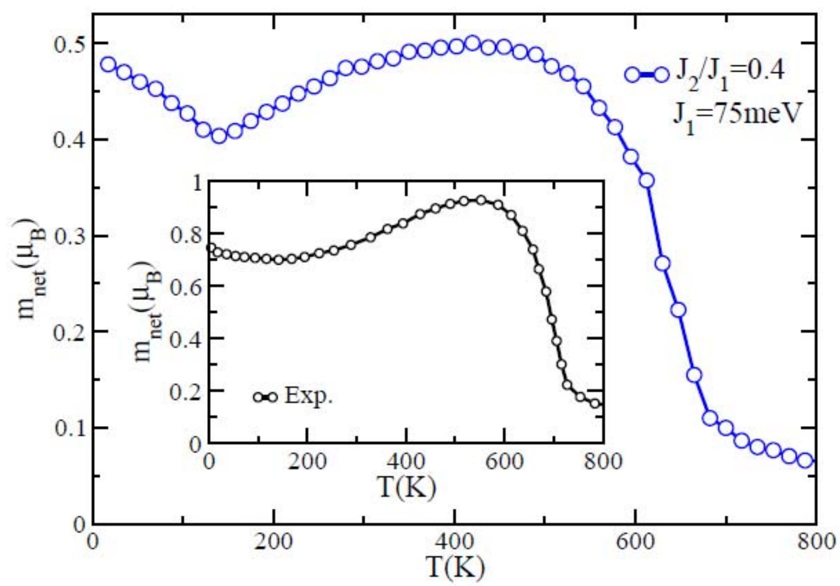
Measurements taken at the National High Magnetic Field Laboratory

J. Soliz, A. Hauser, F.Y. Yang, M. Susner, M. Sumption, P. M. Woodward, (unpublished)

Sr_2CrOsO_6 A canted antiferromagnet

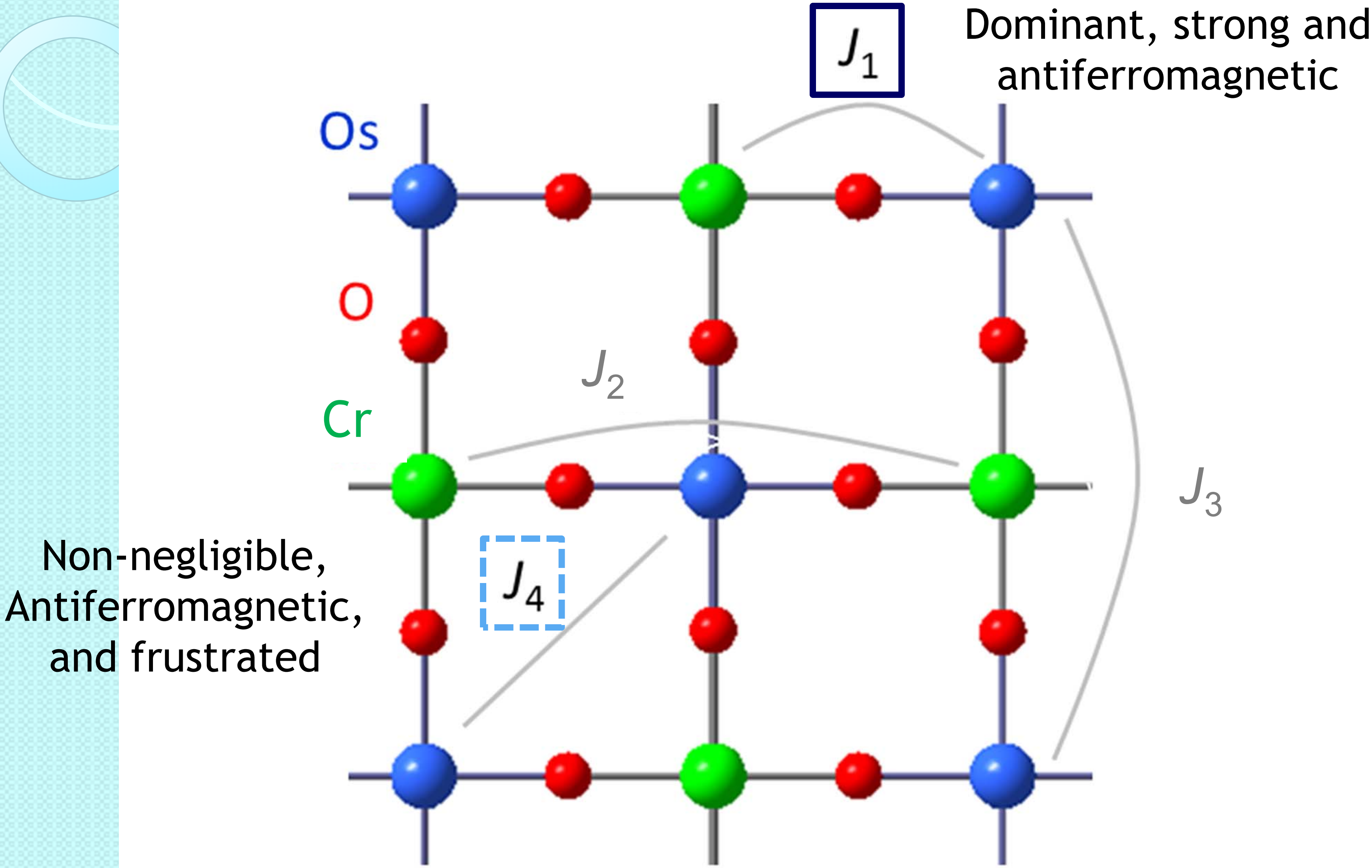


Os—Os superexchange (J_4) is responsible for the unusual M vs. T behavior and at least partially responsible for the net magnetization



Meetei, Erten, Trivedi, Randeria, Woodward, *Phys. Rev. Lett.* **110**, 087203 (2013).

Superexchange interactions (A_2CrOsO_6)



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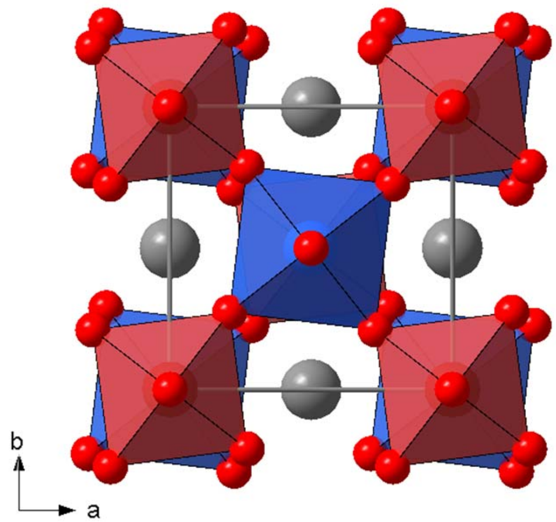
- A_2MOsO_6 with $M = Mg^{2+}$
- A_2MOsO_6 with $M = Cr^{3+}$
- A_2MOsO_6 with $M = Co^{2+}$
- Concluding thoughts

Sr_2CoOsO_6 (d^7–d^2) Structure

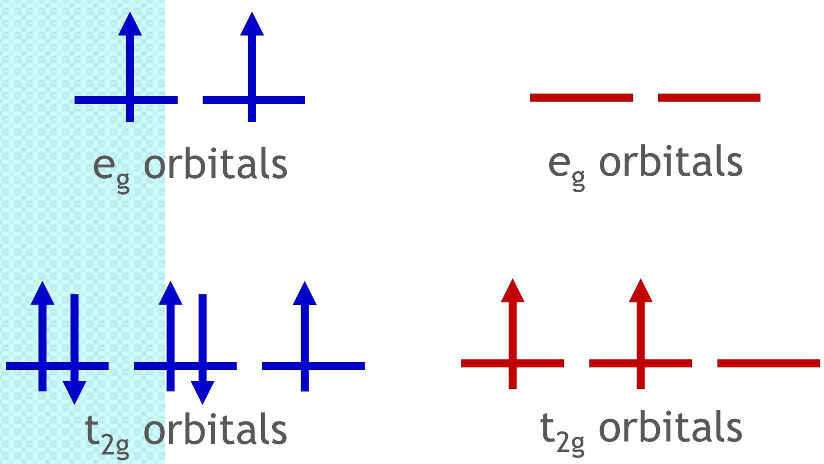


Tolerance Factor = 0.953

Space Group: *I*4/*m* (Tetragonal)

$a^0a^0c^-$ tilting

100% Co/Os ordering



Co^{2+} (d^7) **Os^{6+} (d^2)**

Co^{2+}–O distances (Å)
4×2.038(2), 2×2.052(2)
4×2.031(1), 2×2.050(2) Sr_2MgOsO_6

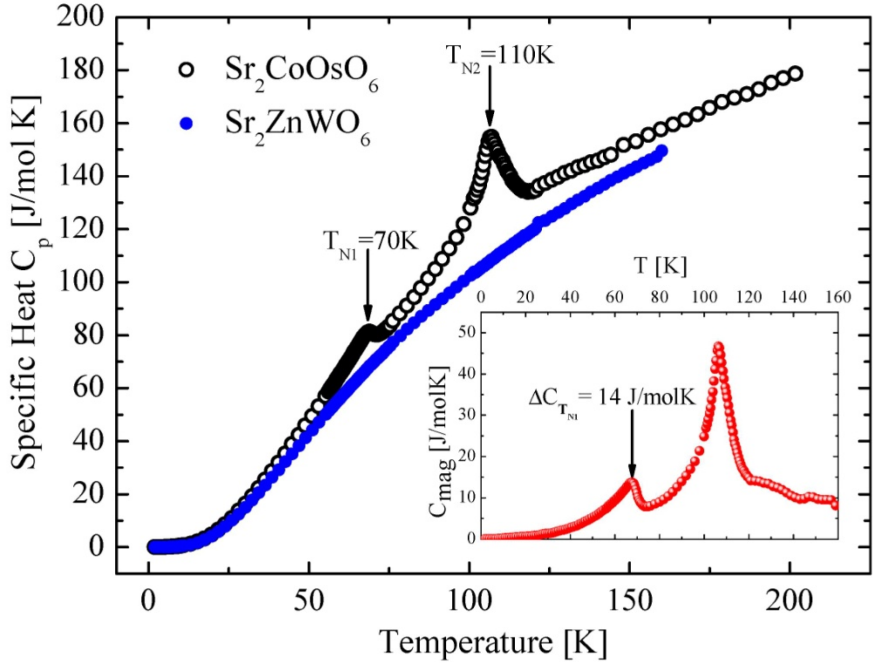
Os^{6+}–O distances (Å)
4×1.915(2), 2×1.927(2)
4×1.910(1), 2×1.939(2) Sr_2MgOsO_6

Co–O–Os angles:
165.83(6)°, 180°
165.30(6)°, 180° Sr_2MgOsO_6

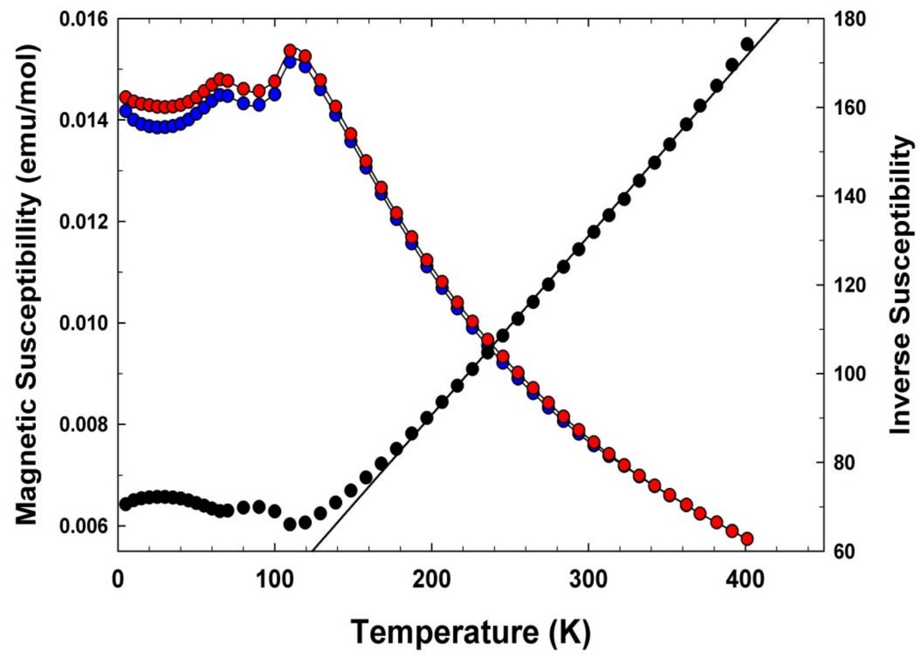
Morrow, et al., *J Amer Chem Soc* **135**, 18824 (2013)

Sr_2CoOsO_6 Phase Transitions

Specific Heat



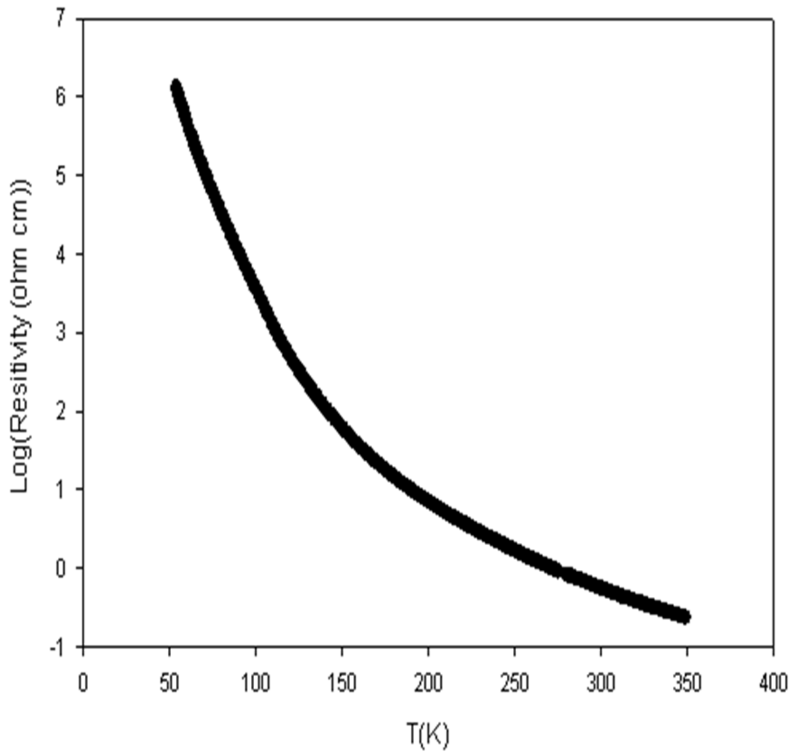
Magnetic Susceptibility

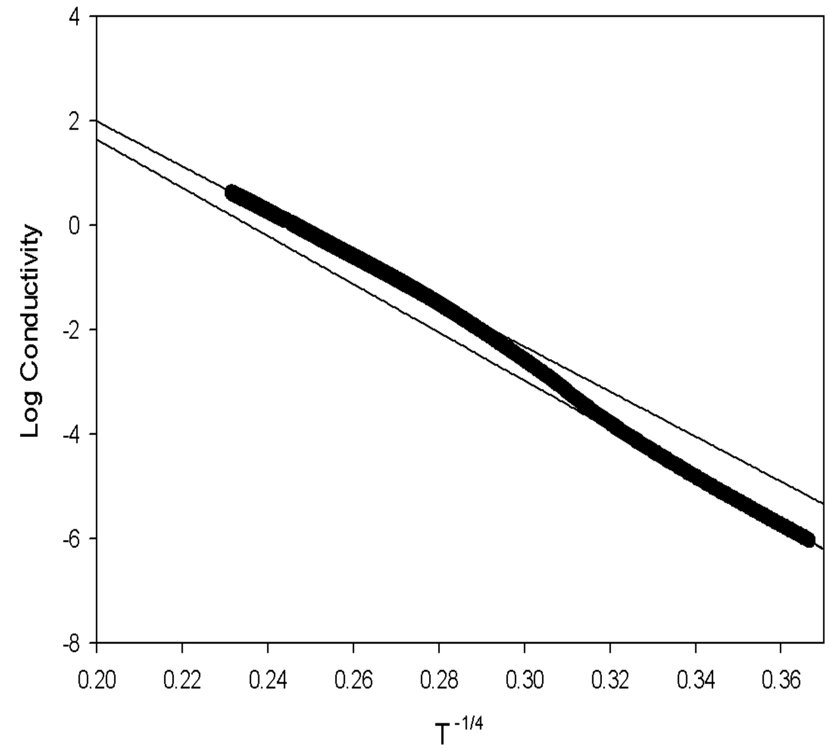


- Antiferromagnetic, T_{N1} = 110 K, T_{N2} = 70 K
- μ_{eff} = 4.45 μ_B/f.u. (spin only μ_{eff} = 4.80 μ_B/f.u.)
- Weiss constant, θ = −51 K

Morrow, et al., *J Amer Chem Soc* **135**, 18824 (2013)

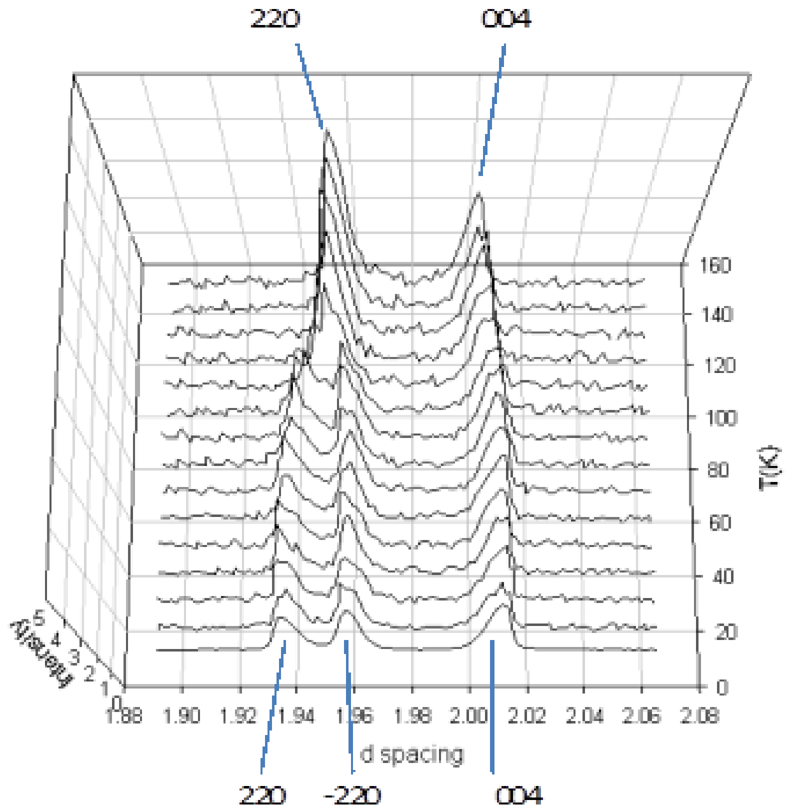
Sr_2CoOsO_6 Resistivity

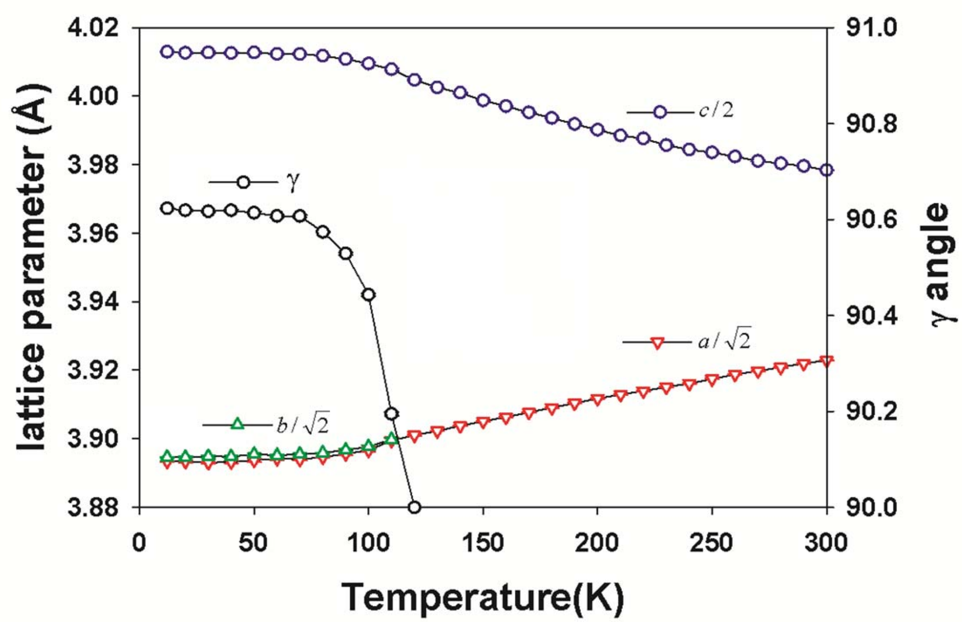




- Variable range hopping $\rightarrow$ localized electrons
- Slight discontinuity at 110 K (phase transition)

Variable Temperature Neutron Diffraction

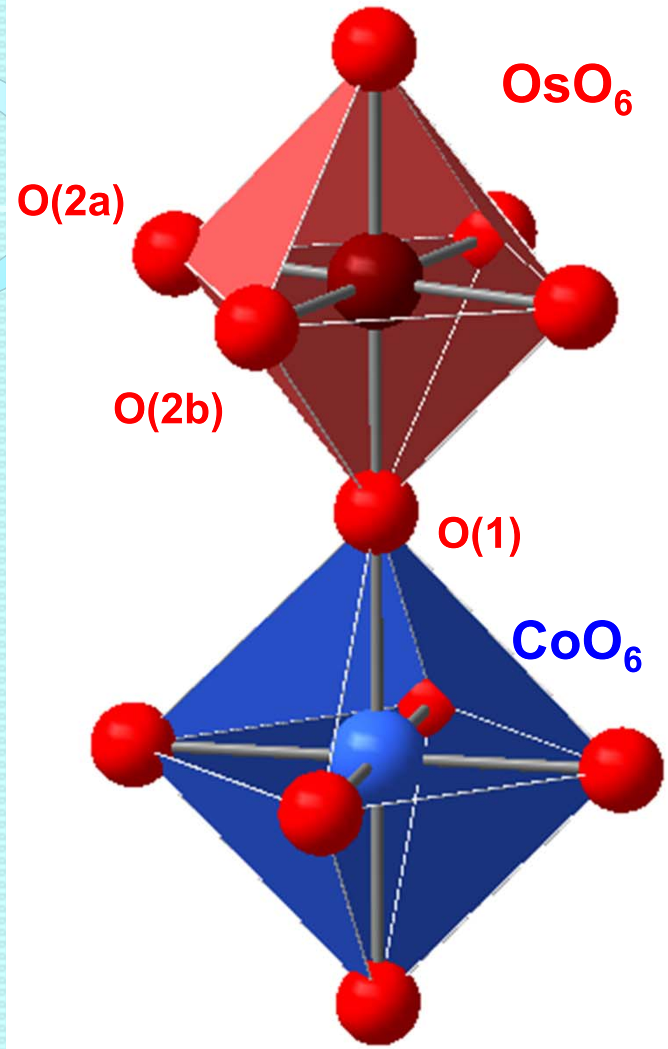


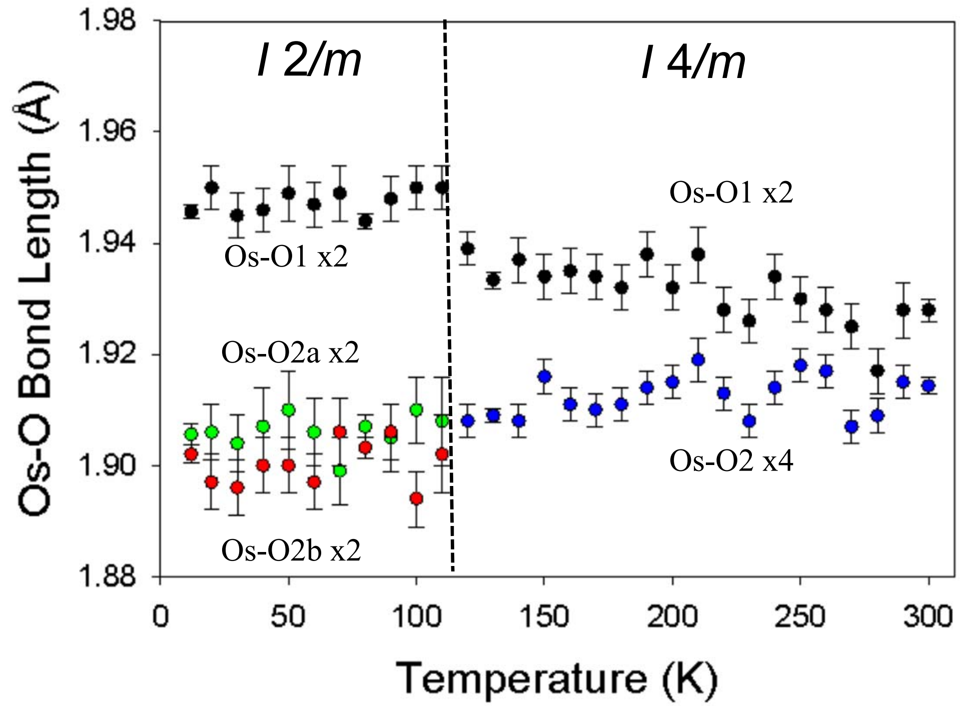


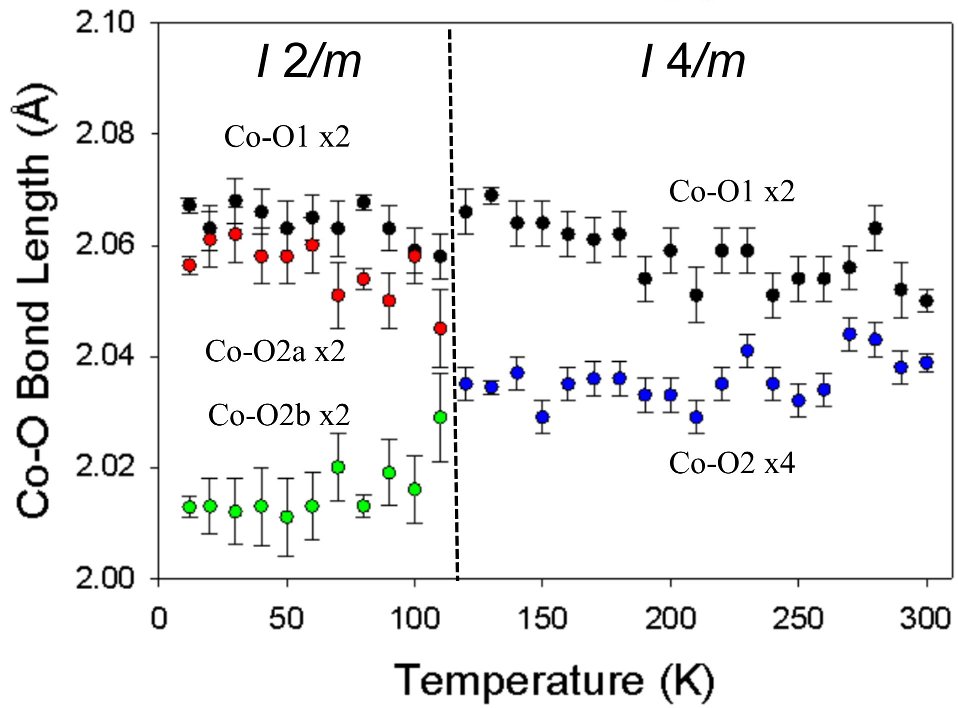
- T > 110 K → Tetragonal, *I*4/*m* ($a^0a^0c^-$ tilting)
- T < 110 K → Monoclinic, *I*2/*m* ($a^0a^0c^-$ tilting + CoO_6 distortion)

Morrow, et al., *J Amer Chem Soc* **135**, 18824 (2013)

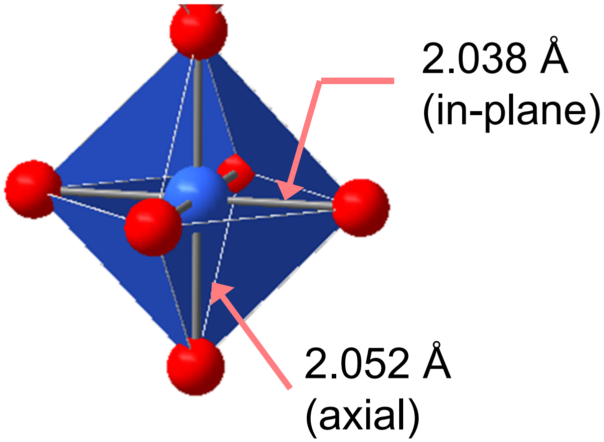
Bond Lengths



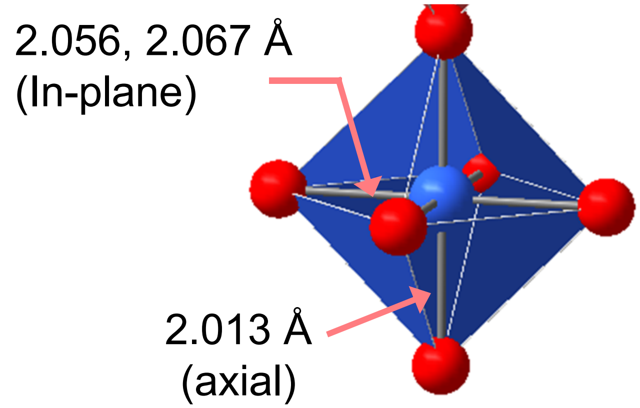


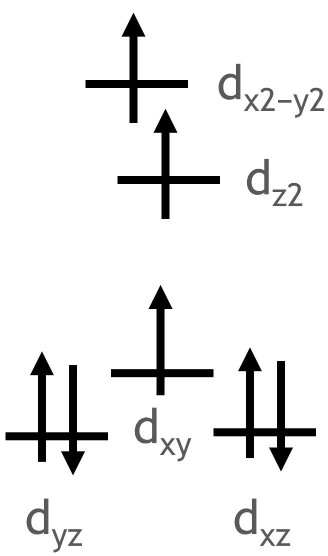


CoO_6 at 300 K

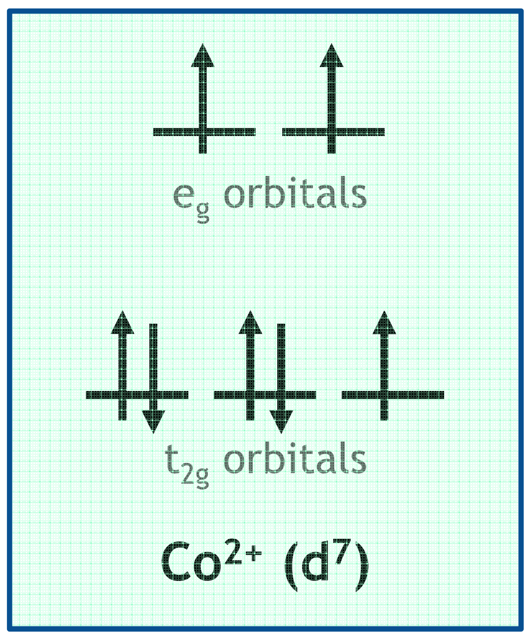


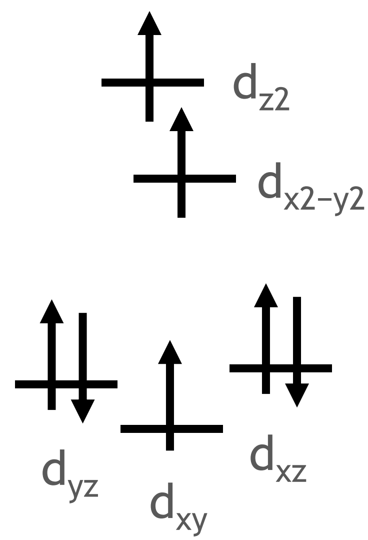
CoO_6 at 12 K





Expected distortion

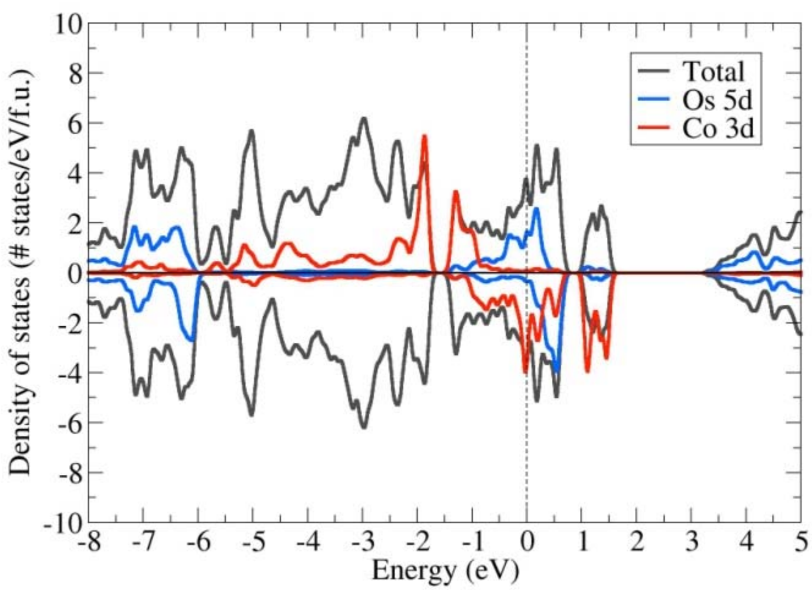




Distortion observed below 110 K

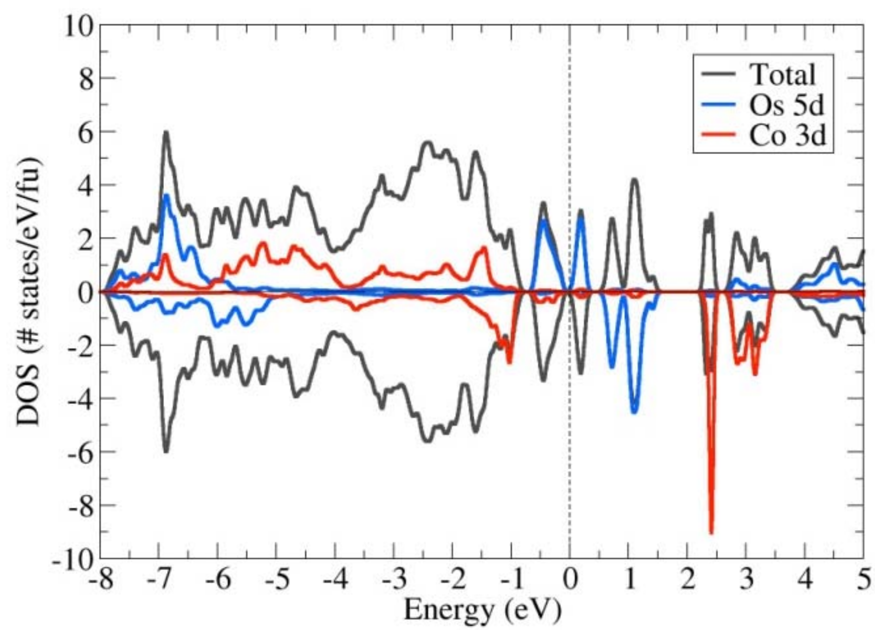
DFT Calculations

GGA



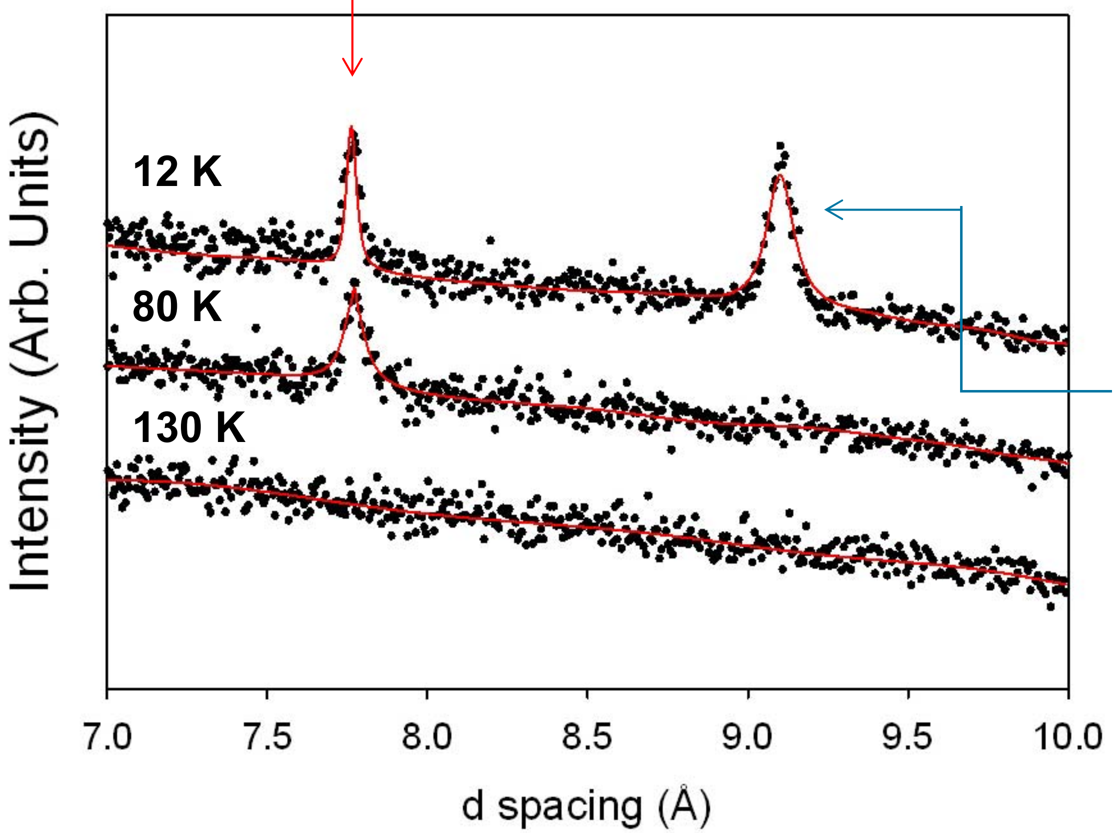
GGA+U

(U_{Co} = 4.1 eV, U_{os} = 2.1 eV)



- Osmium strongly hybridizes with oxygen
- Correlations needed to open a gap
- Os 5d t_{2g} states at the Fermi level

Magnetic Structure (Neutron Powder Diffraction)



T < 110 K

Os^{6+} (d^2) spins order

Os moment = 1.57(5) μ_B (@ 80 K)

Os moment = 1.81(4) μ_B (@ 12 K)

k = (½, ½, 0)

T < 70 K

Co^{2+} (HS d^7) spins order

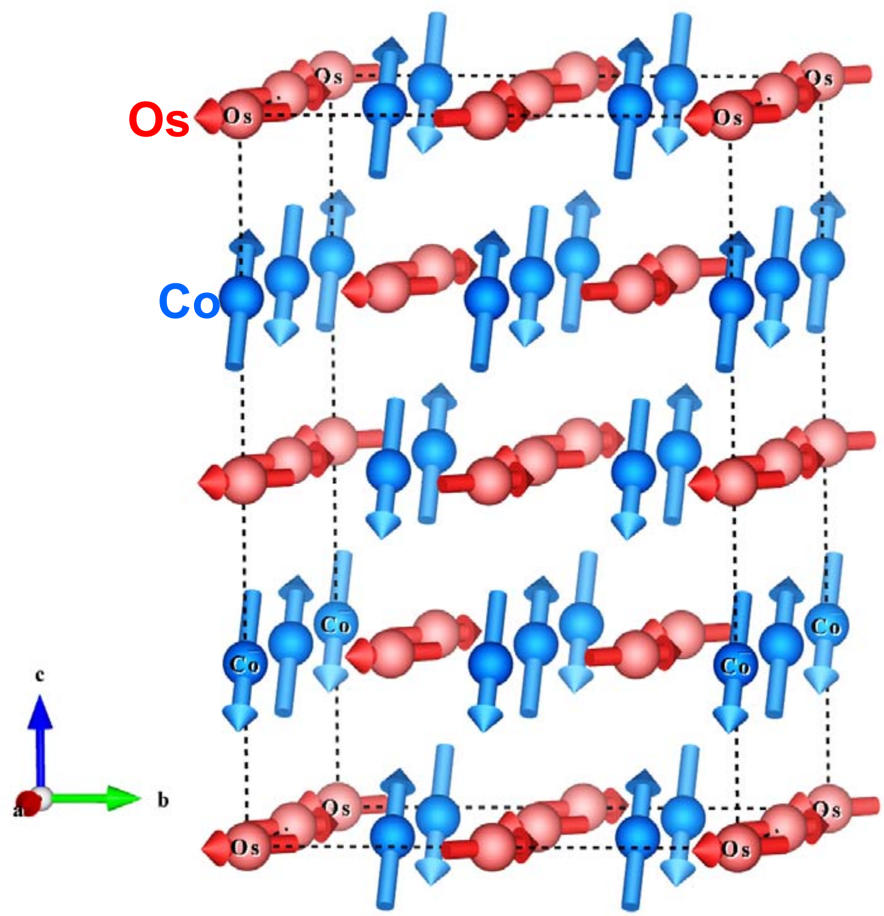
Co moment = 2.90(5) μ_B (@ 12 K)

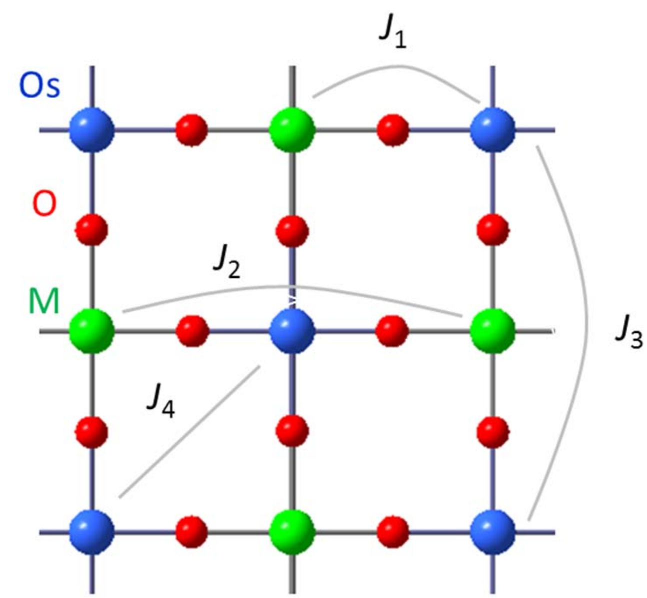
k = (½, 0, ½)

Os and Co spins order independently

Morrow, et al., *J Amer Chem Soc* **135**, 18824 (2013)

Sr_2CoOsO_6 Magnetic Structure

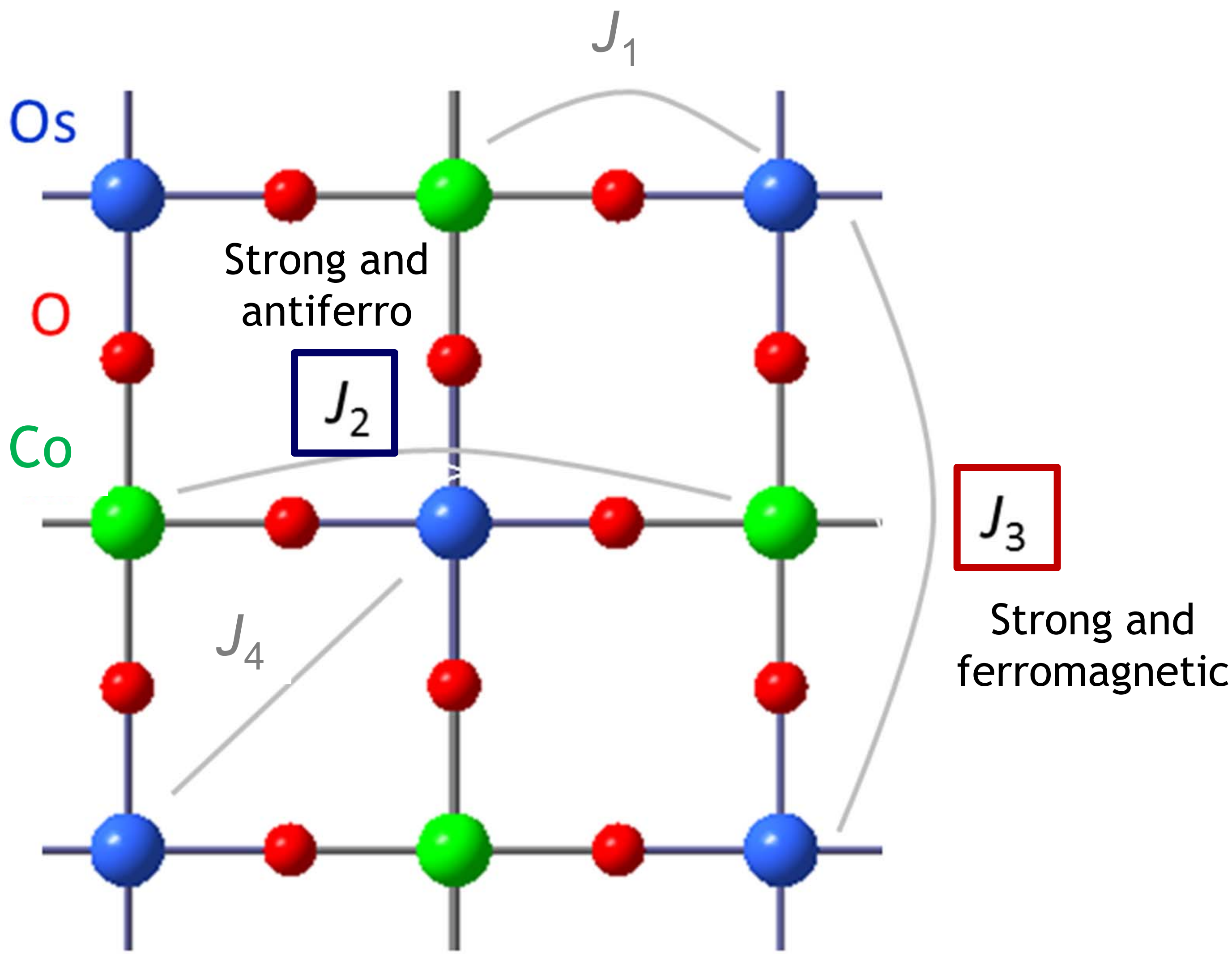




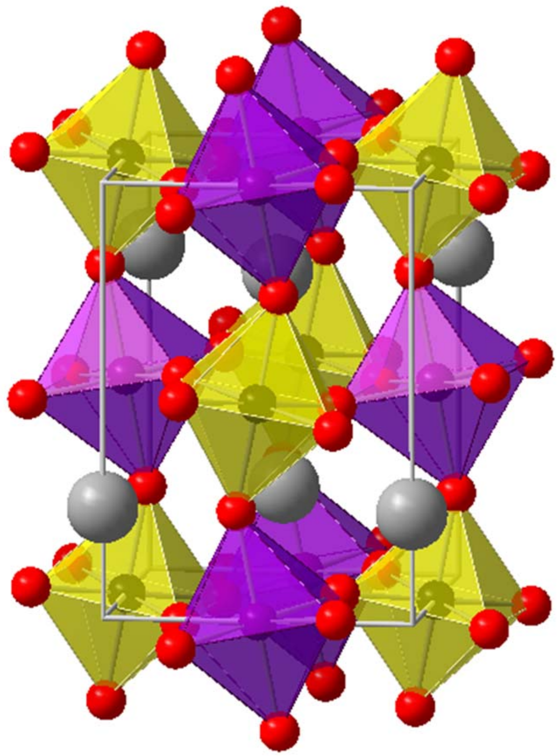
Co–O–Os	$J_1^{eff} = -1.3$ meV
Co–O–Os–O–Co	$J_2^{eff} = -47.2$ meV
Os–O–Co–O–Os	$J_3^{eff} = +20.2$ meV
Os–Os xy-plane	$J_4^{eff} = +0.8$ meV
Os–Os out-of-plane	$J_4^{eff} = -13.4$ meV

The long range J_2 and J_3 interactions are dominant!

Superexchange interactions (Sr_2CoOsO_6)



Ca_2CoOsO_6 (d^7–d^2) Structure



Tolerance Factor: 0.901

Space Group: $P2_1/n$ (Monoclinic)

$a^-a^-b^+$ tilting

100% Co/Os ordering

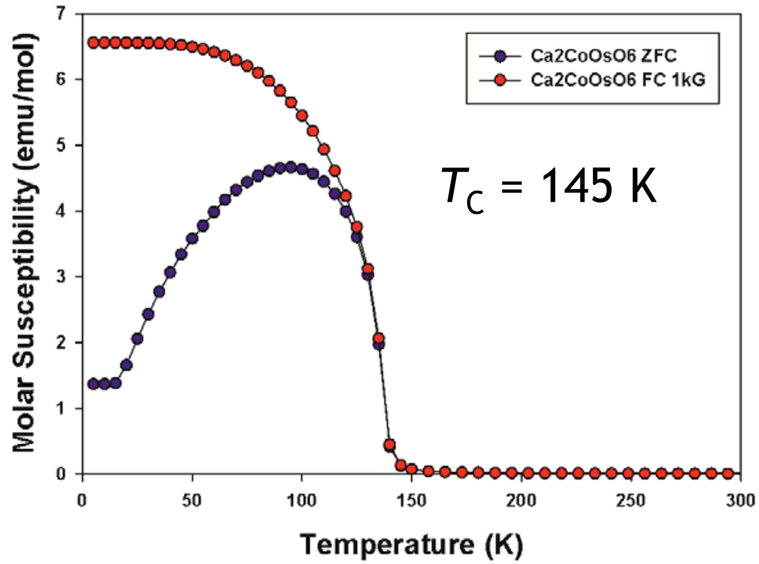
Co^{2+}–O distances (Å)
 2×2.027(2), 2×2.071(2), 2×2.080(2)

Os^{6+}–O distances (Å)
 2×1.926(2), 2×1.932(1), 2×1.935(1)

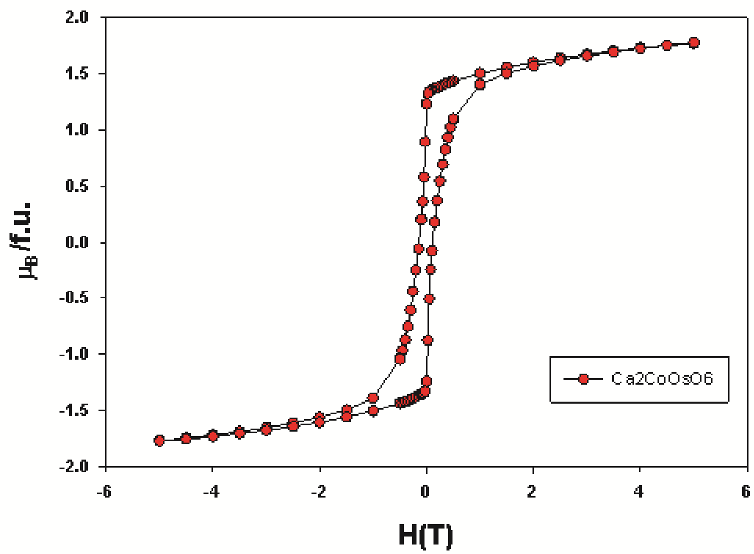
Co–O–Os angles:
 149.9(2)°, 149.0(1)°, 149.9(1)°

How does the increased distortion of the Co–O–Os bond angles impact the competing superexchange interactions?

Ca_2CoOsO_6 Magnetism

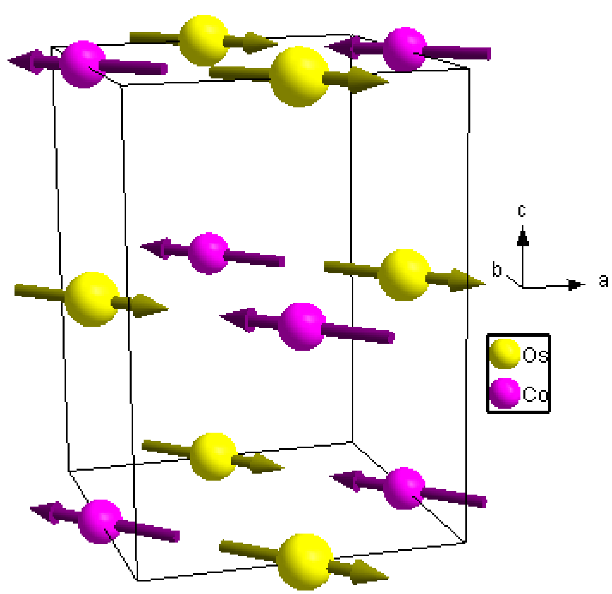


$M_{sat} \approx 1.7\ \mu_B$/fu



Co moment:
2.9(2) μ_B

Os moment:
0.5(2) μ_B



Bending the Co–O–Os bonds stabilizes a **ferrimagnetic** ground state.

J_1 now controls the magnetism!

A_2MOsO_6 Perovskites

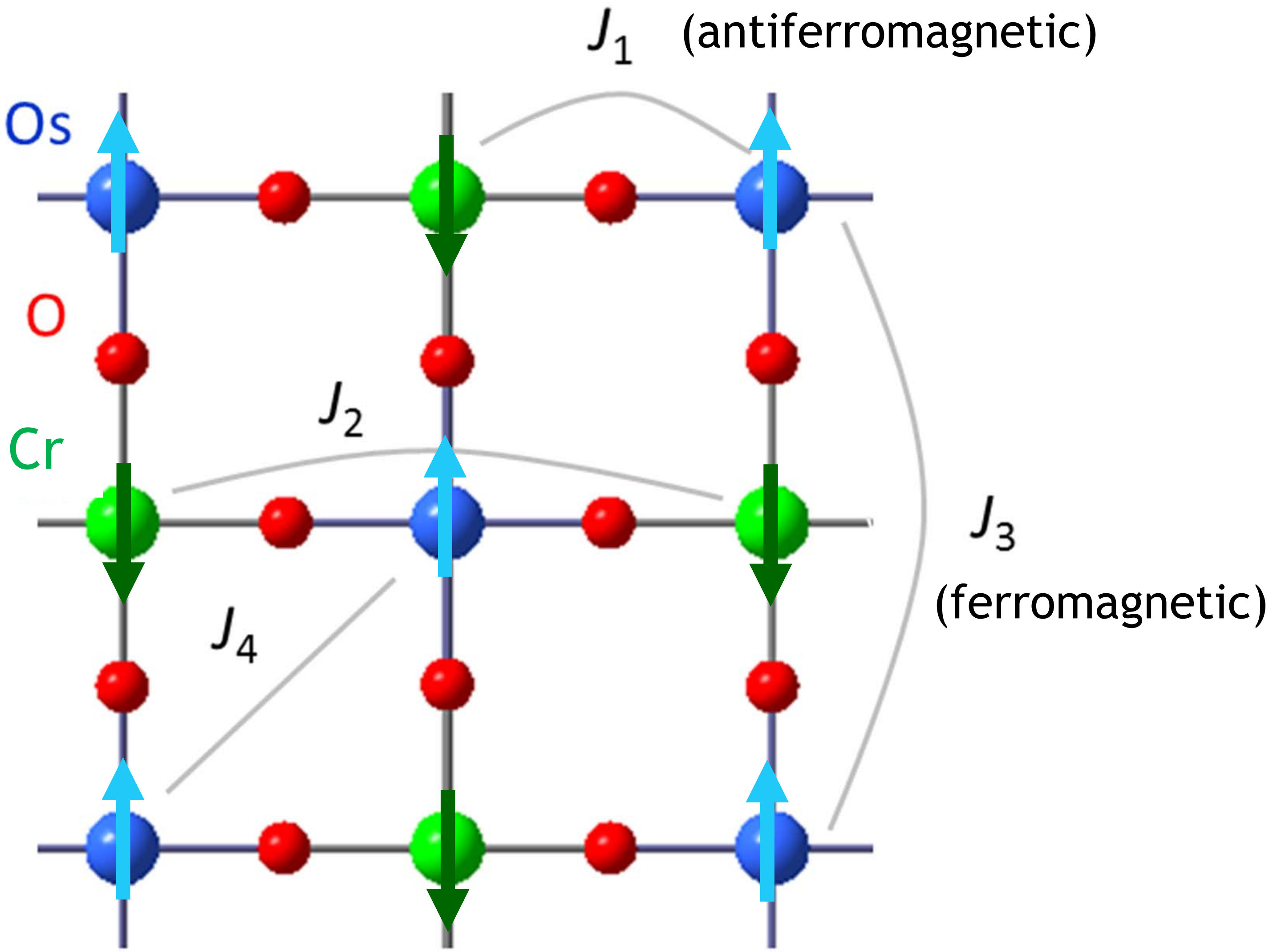
A_2MOsO_6	Tilting	M–O–Os ∠	Magnetism
$d^3 - d^3$			
Sr_2CrOsO_6	$a^-a^-a^-$	170°	FiM, T_C = 720 K
Ca_2CrOsO_6	$a^-a^-c^+$	154°	FiM, T_C = 490 K
$d^5 - d^3$			
Sr_2FeOsO_6	$a^0a^0c^-$	165°, 180°	AFM, T_N = 140, 67 K
Ca_2FeOsO_6	$a^-a^-c^+$	152°	FiM, T_C = 375 K
$d^7 - d^2$			
Sr_2CoOsO_6	$a^0a^0c^-$	166°, 180°	AFM, T_N = 110, 70 K
Ca_2CoOsO_6	$a^-a^-c^+$	150°	FiM, T_C = 145 K
$d^8 - d^2$			
Sr_2NiOsO_6*	$a^0a^0c^-$	163°, 180°	AFM, T_N = 50 K
Ca_2NiOsO_6*	$a^-a^-c^+$	151°	FiM, T_C = 175 K

*Macquart, Kim, Gemmill, Stalick, Lee, Vogt, zur Loye, *Inorg. Chem.* **44**, 9676 (2005).

Outline

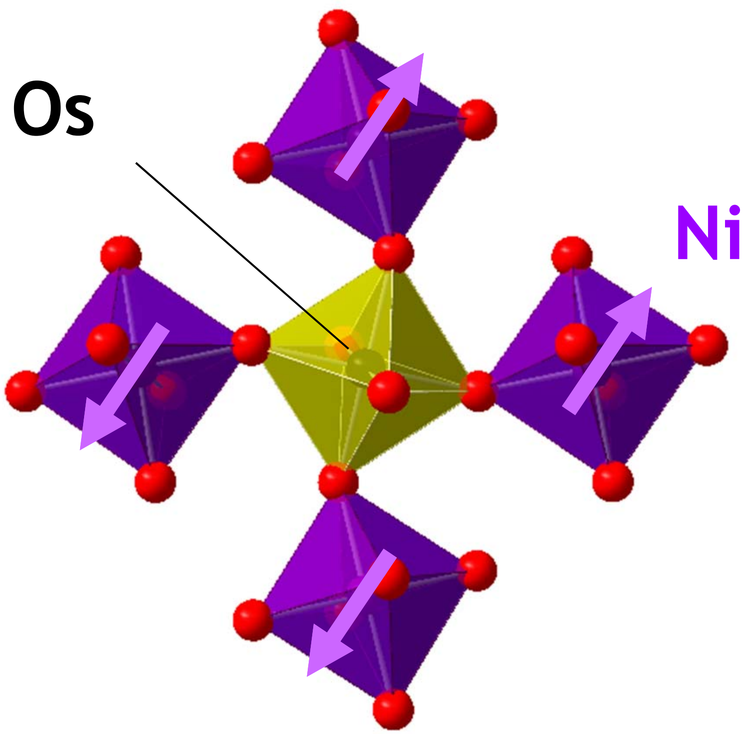
- Introduction
- A_2MOsO_6 with M = Mg^{2+}
- A_2MOsO_6 with M = Cr^{3+}
- A_2MOsO_6 with M = Co^{2+}
- Concluding thoughts

Ferrimagnetism satisfies both J_1 and J_3



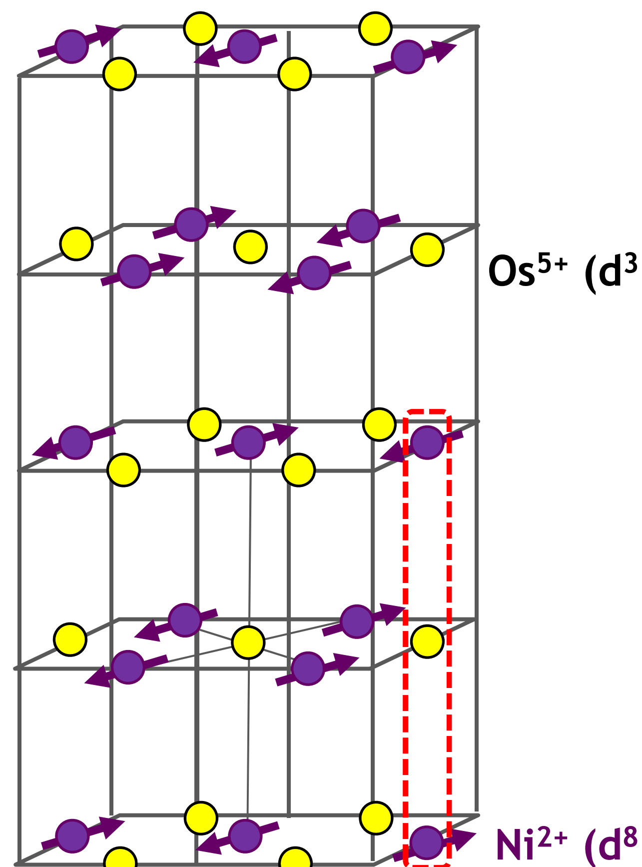
But it **does not** satisfy J_2 or J_4

When J_2 (M-O-Os-O-M) is dominant



If 3d-3d Ni–O–Os–O–Ni bond e_g AFM superexchange is stronger than 3d-5d FM superexchange, it sets up a frustration for the Os spins.

$LaSrNiOsO_6$



AFM

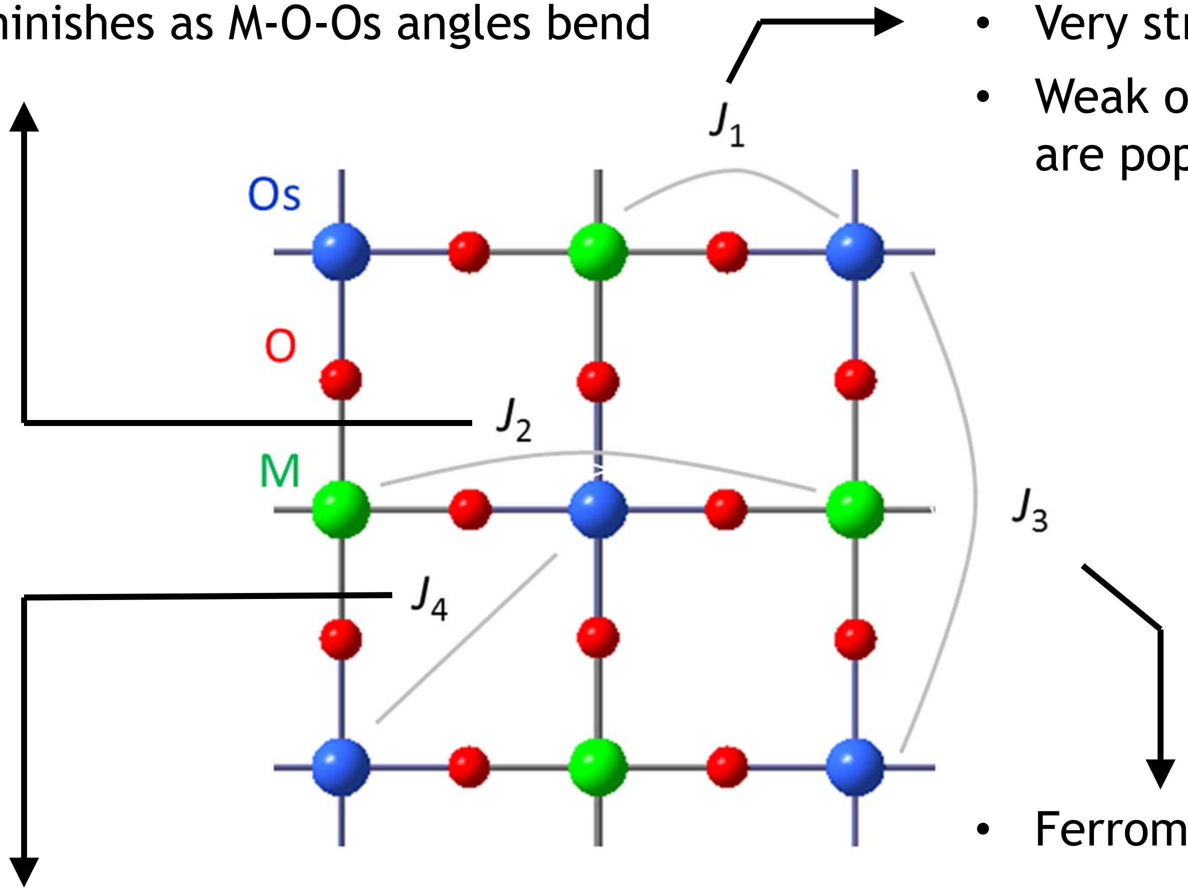
k = (½,0,½)

T_N = 65 K

5d-3d Superexchange Interactions

- Antiferromagnetic
- Diminishes as M-O-Os angles bend

- Always AFM
- Very strong for d^3-d^3 case
- Weak once 3d e_g orbitals are populated



- Ferromagnetic

- Can be relatively strong
- Frustrated topology

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